Thermosetting epoxy reinforced shape memory composite microfiber membranes: Fabrication, structure and properties

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ABSTRACT

The thermosetting epoxy-based shape memory composite microfibers are successfully fabricated by means of coaxial electrospinning. The PCL/epoxy composite fiber shows core/shell structure, in which epoxy as the core layer is for an enhancing purpose. By incorporating epoxy and PCL, the mechanical strength of composite fibers is greatly reinforced. The deformation is via the heating and cooling process, and the shape memory effect can be demonstrated from the micro level to the macro level. The whole shape recovery performance takes only 6.2 s when triggered by the temperature being at 70 °C. The porosity of woven microfibers changes in response to temperature. In addition, the PCL/epoxy composite microfiber membranes are analyzed in an in vitro cytotoxicity test, which proves that PCL as the shell layer provides the composite microfibers potential capabilities in biomedical science.

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1. Introduction

Shape memory polymers (SMPs), due to their special ability to remember deformed shapes and recover these original shapes in response to external stimuli, such as temperature, electricity, magnetism and solutions are attractive in a wide array of fields [1–5]. Compared to shape memory alloys (SMAs), the advantages of SMPs include large deformation, light weight, large recovery ability, lower cost as well as superior process ability [2]. And their stiffness can be changed between the thermoplastic glass and the elastomer when actuated by temperature. SMPs filled with different particles and fibers can realize the multifunction and reinforcement which has been demonstrated in previous research [6]. On the basis of a fixed phase structure, SMPs are classified into thermosetting and thermoplastic SMPs [7]. Epoxy, as a kind of thermosetting SMPs with high strength and large deformation, is successfully used in aerospace, automobiles, robotics and so on [8,9]. A large variety of polymers have been added into epoxy matrix to realize different functions. In previous reports, some researchers combine epoxy with polycaprolactone (PCL) to realize the multifunction of composites. For instance, Mather and coworkers [10] have synthesized a shape memory composite, through incorporating non-woven PCL fibers into an epoxy-based SMP matrix. Such a composite is able to

display triple-shape memory effect because it possesses two transition temperatures T_m and T_g respectively. Luo et al. [11] reported that they prepared electrospun thermoplastic PCL fibers which were distributed in a shape memory epoxy matrix. The mechanical damage was capable of being self-healed via heating. Oh and co-workers fabricated the meta-aramid/epoxy fibers with core/shell structure, the thermal and mechanical performances of which were investigated in the adhesive composites [12,13]. Although epoxy has been developed in so many fields, the applications of epoxy resin are still limited by the properties of itself, especially the application size at the micro- or nano- level. In addition, it cannot be used in biomedicalfield. In order to obtain the micro-size epoxy which can be used in biomedical fields, we design a system cooperating the thermosetting epoxy and thermoplastic PCL together through electrospinning.

Electrospinning, being recognized as an efficient technique, has been utilized for fabrication of fibers with micro-size or nano-size diameters [14–16]. Recently, an increasing number of SMPs have been electrospun into fibers, such as polycaprolactone [17,18], polyurethane [19,20], as well as Nafion [21,22], which will have potential application in the biomedical field [23,24]. PCL is a very attractive polymer, advantages of which include biodegradability, low cost, availability and physicochemical properties (semicrystallinity, hydrophobicity) tuned easily through chemical modification or copolymerization with other monomers [17]. The cross-linking of homo- and co-polymers often leads to superior

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mechanical performance of these materials, such as high modulus and dimensional stability. Besides, during the last decade, several strategies for the crosslinking of PCL derivatives have been taken. Very recently, it has been reported that PCL networks can exhibit excellent shape memory properties including shape fixity and recovery ratios [18]. Therefore, PCL shows biodegradability, biocompatibility, shape memory effect and in some cases, recyclability. These advantages open up new perspectives for biomedical applications (degradable stents and implants, drug carrier matrices, hard and soft tissues engineering, stem cell therapy, etc.) or for recyclability and reprocessing of cross-linked materials [25,26].

Coaxial electrospinning, being used to obtain fibers with more than one compound material, can turn some materials without spinnability into fiber structure to develop the properties and applications [27,28]. As we all know, thermoset polymers are not able to be electrospun into fibers because of the poor spinnability. In order to solve these problems, we design a kind of core/shell structure composite fibers system in which epoxy is the core layer and PCL is the shell layer. PCL as a template is easy to draw the epoxy into fibers. To electrospin epoxy into fibers is a challenge that has not been reported. The core/shell composite fibers have a reinforced inner layer with good mechanical properties capable of improving the PCL's low strength and stiffness. On the other hand, the outside layer PCL brings epoxy into potential biomedical applications.

In this paper, we describe a kind of core/shell composite fiber. PCL as shell material and epoxy as core material were electrospun into microfibers by co-electrospinning method. This new system was characterized by SEM, TEM, DSC, DMA and vitro cytotoxicity test, etc. to analyze the morphology, structure, thermal and mechanical properties, as well as biological behavior. Shape memory effect was also demonstrated from micro and macro perspectives. Thus, the strong and flexible polymer composite fiber films are developed and are promising for applications in smart materials and structures, especially in tissue engineering in the future.

2. Materials and experiment

2.1. Materials

Polycaprolactone (PCL, Mw = 50,000) was purchased from Perstorp UK. Benzophenone ($C_{13}H_{10}O$) as the UV agent, dichloromethane (CH_2Cl_2) and dimethylformamide (DMF) as the solutions were purchased from Tianjin guangfu fine chemical research institute and used as received. Epoxy-based shape memory polymer specimens were synthesized according to the procedure reported by Wu et al. [29]. Epoxy SMPs were fabricated by mixing epoxy resin and hardener which was 35 wt.% for EP06. Mouse schwann cells were purchased from American Type Culture Collection (ATCC), USA. CCK-8 was purchased from Dojindo, Japan. All biological experiment procedures were approved by the Ethics Committee of the First Affiliated Hospital of Harbin Medical University.

2.2. Electrospinning of PCL/epoxy composite microfibers

The PCL/epoxy composite microfibers were prepared as displayed in Fig. 1. CH_2Cl_2 and DMF were mixed together with a volumetric proportion of 4:1. PCL was dissolved in the mixed solvent with a concentration of 15 wt.%. And the 10 wt.% UV initiator benzophenone was added in the mixture. The polymer solution was stirred on a magnetic stirrer at room temperature until well mixed. Fig. 1a shows the schematic illustration of electrospinning setup to fabricate the core–shell fibers. The syringes we used for epoxy and PCL were 1 mL and 2.5 mL, respectively. The electrospinning parameters were listed in the following: the needle size was an inner diameter of 100 ím and outer diameter of 200 ím; the needle tip to collector distance and applied voltage were 18 cm and 15 kV, respectively. The feed rate of PCL was 0.002 mm/s and the feed rate of epoxy was 0.0005, 0.0008, 0.001 and 0.002 mm/s, respectively. The feed ratios between PCL and epoxy were named as 1:1, 2:1, 2.5:1, and 4:1, respectively. During the electrospinning process, the diameters of core fibers varied with the changes of the flow rate of epoxy. The composite microfibers specimens (as shown in Fig. 1b and c) were electrospun on aluminum for 30 min and cured at 70 °C for more than 75 h in the oven. Fig. 1d shows the morphology of the electrospun composite microfibers. During the electrospinning process as shown in Fig. 1e, the UV lamp, the wavelength of which was 365 nm (the power was 100 W), was used to radiate the PCL to form the networks for shape memory effect [30].

2.3. Characterization

SEM images of PCL/epoxy composite microfibers were collected by scanning electron microscopy (SEM, Quanta 200FEG). The specimens were coated with a thin layer Au metal for 10 min.
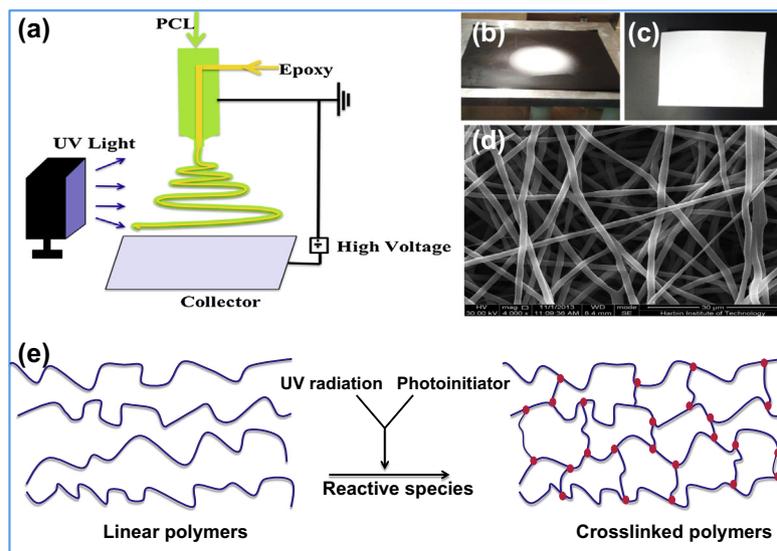

Fig. 1. Schematic illustration of co-electrospinning and UV photoinitiato process. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Transmission electron microscopy (TEM, FEI, Tecnai G2 F30) was performed to analyze the core–shell structure of PCL/epoxy composite microfibers. The sample was electrospun on the 200 mesh copper net for 5 s.

Differential scanning calorimetry (DSC) was employed to characterize the thermal property of PCL and PCL/epoxy composite microfibers on the METTLER TOLEDO instrument (DSC1). The measurement was carried out in air from 0 °C to 80 °C at a heating rate of 10 °C/min.

Thermal stabilization property was tested by thermo gravimetric analysis (TGA, Mettler Instruments), which was conducted from 25 °C to 600 °C with a heating rate of 10 °C/min and an air flow rate of 30 mL/min.

Strain–stress test was measured using nanotensile, a commercial nanotensile testing system (Nano UTMTM Universal Testing System T150, Agilent Technologies).

Nitrogen adsorption (Micromeritics ASAP 2020) was applied to the analysis of the specific surface area and pore distribution.

The thermal–mechanical performance was studied on dynamic mechanical analyser (DMA, Mettler Instruments) with a heating rate of 5 °C/min at a constant frequency of 1 Hz. The resulting PCL/epoxy composite membranes was cut into 12 mm × 4 mm × 0.18 mm (length × wideness × thickness).

Shape recovery ratio was calculated by Eq. (1) [31]:

$$R_r = \frac{\theta_i - \theta_t}{\theta_i - \theta_e} \times 100\% \tag{1}$$

where θ_i, θ_e are the initial deformation angle of the fixed sample, the deformation angle at a given time t, and the angle at the equilibrium state, respectively.

2.4. Cytotoxicity assays

The CCK-8 assay was used to evaluate the cell availability [32]. Single cell suspensions of 20,000 schwann cells in 100 μL Dulbecco's Modified Eagle's Medium (DMEM, Invitrogen, with 4.5 g/L L, D-glucose and 4.5 M L-glutamine) which was supplemented with 10 wt.% FBS and 1 wt.% penicillin–streptomycin (Invitrogen) were added in the 96-well plate and incubated for 24 h at 37 °C under 5% CO$_2$. 10 μL of different material extracting solutions (material/PBS, 1 g/1 mL, w/v) were added and incubated for 24, 48, 72 and 96 h respectively. The cell culture medium was changed every 2 days. 10 μL of CCK-8 solution was added to each well and incubated for 1 h. To avoid forming bubbles deserves great attention. The optical density (OD) of each well was measured by the Biotek microplate spectrophotometer (Winooski, VT) at 450 nm ($n = 6$). Three parallel specimens were tested each time.

Both PCL and PCL/Epoxy membranes were cut into a circular shape (0.5 cm × 0.5 cm) to the bottom of a 24-well plate and each well has 4 pieces of samples. 400 μL of DMEM and 40 μL cell suspension were added and cultured in the incubator (37 °C, 5% CO$_2$) for 24, 48, 72 and 96 h respectively. The cell culture medium was changed every 2 days. 10 μL of CCK-8 solution was added to each well and incubated for an additional 1 h. The optical density (OD) of each well was measured by the Biotek microplate spectrophotometer (Winooski, VT) at 450 nm ($n = 6$).

All values were expressed as mean ± SEM. Statistical significance was determined using the Student's unpaired t test. A p value <0.05 was considered statistically significant.

3. Results and discussion

3.1. Microstructure and morphology of microfibers

The effect of the applied voltage was investigated on the morphology of composite microfibers fabricated by coaxial electrospinning. Previous work had demonstrated that PCL was easily electrospun into fibers [15]. However, epoxy as a kind of thermoset polymer did not have the spinnability. The composite fibers were formed if the epoxy could be drafted by PCL liquid. Applied voltage produced charges on the droplet liquid when the electrical field was strong enough, which induced the composite jets to form the fibers.

During the coaxial electrospinning process, the core and shell fluid should have the appropriate feed rate. The feed rate was a key factor to the formation of the composite fibers. In general, the feed rate of the shell was faster than that of the core within a reasonable scope. Fig. 2 shows the morphology of PCL/epoxy composite microfibers with different feed rates. Fixing the feed rate of PCL at 0.002 mm/s, the feed rate of epoxy was adjusted to 0.002, 0.001, 0.0008, and 0.0005 mm/s, respectively. SEM images indicate that the resultant fibers are smooth and uniform except Fig. 2a. It was clear that the same feed rate of shell and core may lead to the shell layer PCL electrospinning alone. The slower the feed rate of epoxy we used, the more continuous the fibers we obtained. The shell liquid was drafted by the electrical field, and the core solution was stretched by frictional force. This system formed the composite fibers because the incompatible system could effectively avoid the mixing, which may lead to the more complete core–shell structure.

Cores–shell composite microfibers made of two identical polymer solutions were obtained by a type of co-electrospinning experiment. As shown in Fig. 3a–d, TEM investigations of the PCL/epoxy composites fibers exhibit obvious contrasts between core and shell, and clearly prove that composite fibers have the core/shell structure. It can be seen from Fig. 3a and b, the diameter of total fiber is about 1200 nm, and the core layer is approximately 800 nm. And Fig. 3c and d shows that the diameter of the composite fiber is about 750 nm, and the core diameter is about 150 nm.
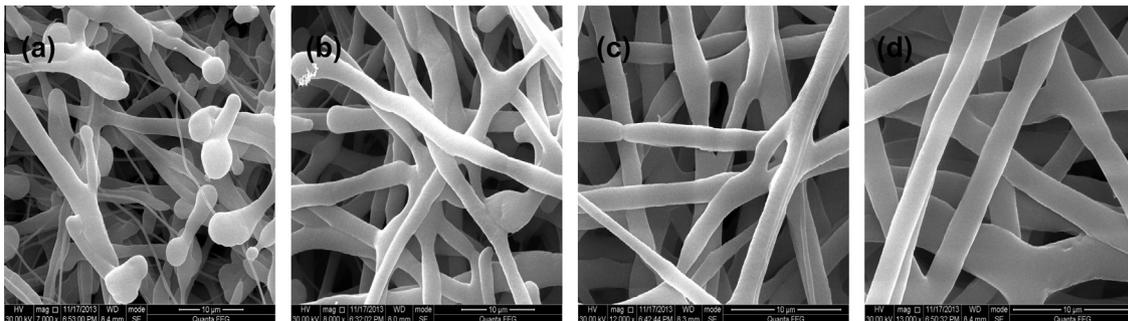

Fig. 2. SEM images of PCL/epoxy microfibers with different flow rates: (a) epoxy = 0.002 mm/s, PCL = 0.002 mm/s; (b) epoxy = 0.001 mm/s, PCL = 0.002 mm/s; (c) epoxy = 0.0008 mm/s, PCL = 0.002 mm/s; (d) epoxy = 0.0005 mm/s, PCL = 0.002 mm/s.
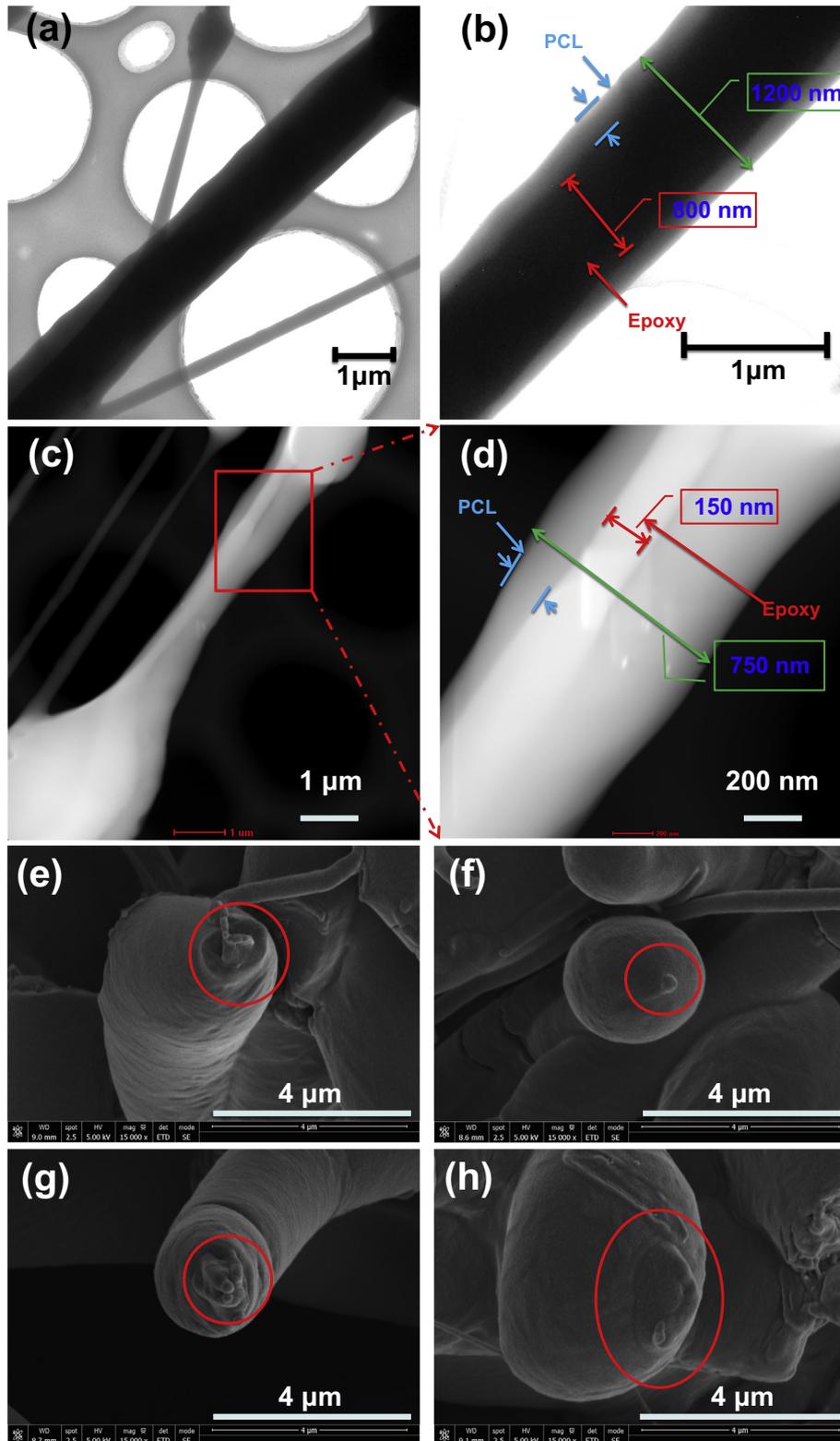
Fig. 3. (a)–(d) TEM images of PCL/epoxy composite microfibers with core/shell structure and (e)–(h) SEM images of cross-section of PCL/epoxy fibers. (a) and (b) Epoxy = 0.002 mm/s, PCL = 0.002 mm/s and (c)–(h) epoxy = 0.0005 mm/s, PCL = 0.002 mm/s. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Furthermore, SEM images of the cross-sections of composite fibers are shown in Fig. 3e–h, which also demonstrate the core/shell structure of PCL/epoxy fibers and the diameter of core layer and composite fiber are varying even in the same electrospinning condition. During the electrospinning process, the diameters of core

fibers varied with the changes of the flow rate of epoxy. The volume fractions between epoxy and PCL with feed ratios of 1:1, 2:1, 2.5:1, and 4:1 were 26.6%, 13.3%, 10.68% and 6.67%, respectively. The solid content of PCL after 30 min were 0.2623 g and the solid contents of epoxy varied from 0.27 g to 0. 018 g with
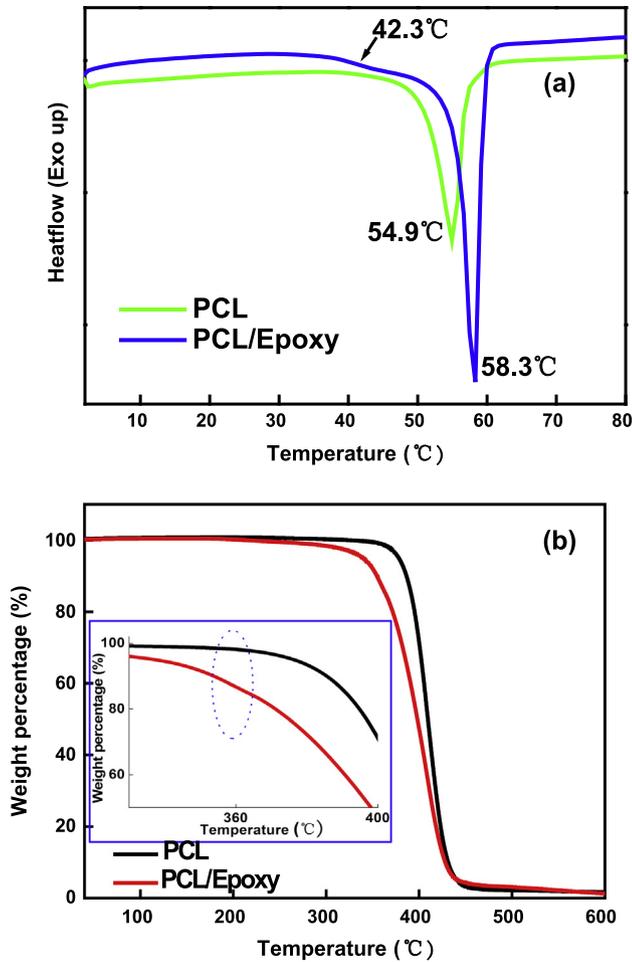
Fig. 4. DSC (a) and TGA (b) curves of PCL and PCL/epoxy microfiber membranes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

transition at lower temperature (42.3 °C) was belonged to the glass transition of epoxy. This result also indicated that core layer and shell layer were two phases independently, which was of advantage to obtain the composite fibers with core–shell structure. It is consistent with the SEM and TEM results.

TGA tests were carried out for pure PCL and PCL/epoxy composite fibers. As shown in Fig. 4b, the TGA curve of PCL shows a weight loss which attributes to the decomposition of cross-linked PCL between 350 °C and 450 °C [18]. For the PCL/epoxy composite curve, there were two weight loss steps (inserted picture). The weight loss between 300 °C and 350 °C was the decomposition of epoxy [29]. And the other weight loss between 350 °C and 450 °C belonged to the decomposition of PCL. From the weight loss, it was demonstrated that the composite fibers were successfully fabricated and possessed stable thermal properties, which were determined by the network structure.

3.3. Mechanical properties analysis

Dynamic mechanical performance was used for evaluating shape memory properties, which was conducted by using DMA. Specimens for the test were cut into 12 mm × 3 mm × 0.5 mm dimensions. As shown in Fig. 5a, it is observed that the modulus of two samples decreases from 40 °C to 60 °C. Storage modulus for PCL/epoxy composite fiber membranes was 92 MPa, which increased compared with that of pure PCL. It was worth noting that
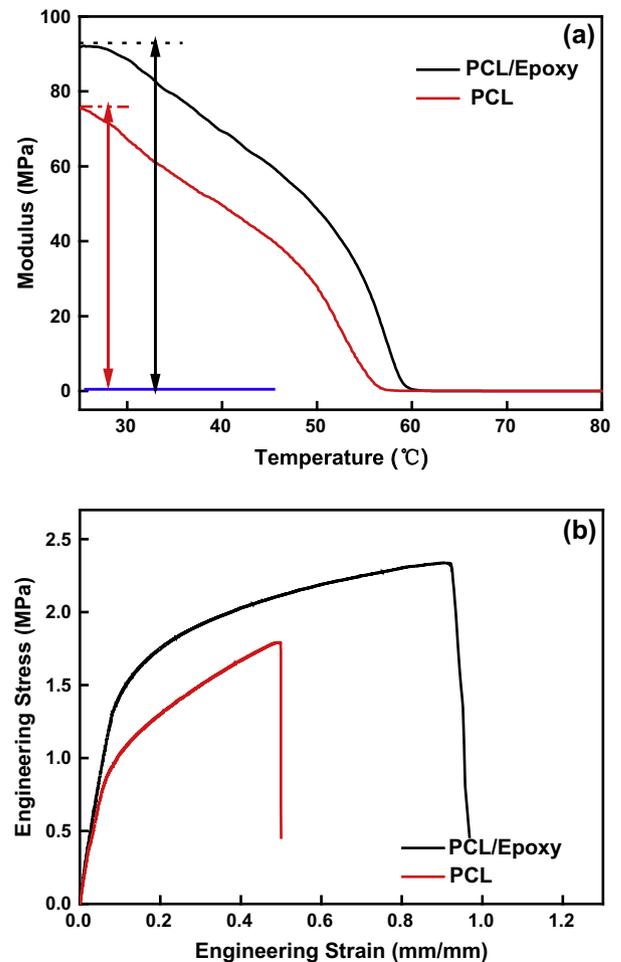
the feed ratio change. It was important to stress here that the epoxy resin solution could not form fibers by itself in the electrospinning process. However, through co-electrospinning, the epoxy fibers were prepared. PCL (shell layer) as a template for the formation of epoxy fibers (core layer) played a key role in the process of electrospinning. The non-electrospinnable materials were related to the properties and electric stress. There was a composite Taylor cone formed at the needle tip during the coaxial electrospinning process. And these two different polymers that were immiscible generated the microphase separation structure. This phenomenon has been explained in the previous reports [10,11]. The co-electrospinning process could be used to make non-electrospinnable materials like epoxy into fibers by using a good fiber shell layer. It also resulted in a novel composite system for non-spinnable component.

3.2. Thermal properties analysis

The thermal properties of electrospinning composite microfibers were tested by DSC. It can be seen from Fig. 4a that there is a decalescence peak in over 55–60 °C, the melting temperature of PCL, which is of importance to shape memory properties of electrospinning fiber membranes. Compared with the PCL, the position of absorption peak for PCL/epoxy slight shifted towards a higher temperature range, which proved that the melting temperature of composite fiber membranes increased. In addition, the step

Fig. 5. DMA curves (a) and strain–stress curves (b) of PCL and PCL/epoxy microfiber membranes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
The Young's modulus (E), offset yield strain (ε_y), fracture strength (F_s), and fracture strain (ε_f) of PCL and PCL/epoxy membranes.

Samples	E (GPa)	ε_y (mm/mm)	F_s (MPa)	ε_f (mm/mm)
PCL membranes	0.016 (0.0007)	0.024 (0.0035)	1.21 (0.092)	0.56 (0.059)
PCL/epoxy membranes	0.021 (0.0014)	0.028 (0.0021)	1.48 (0.075)	0.95 (0.064)
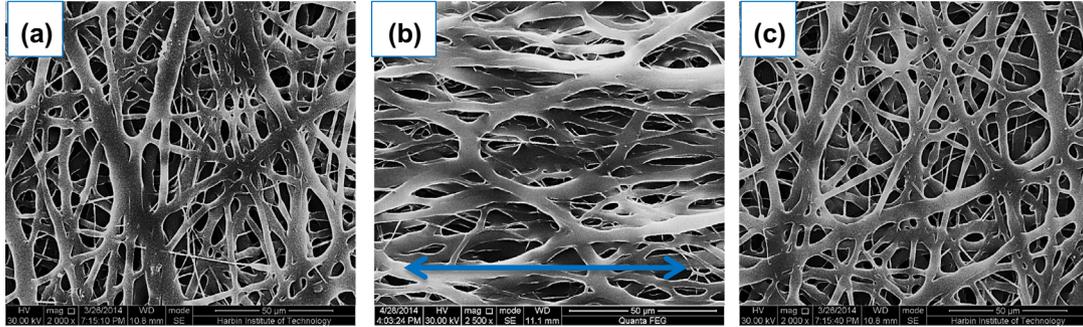
Fig. 6. SEM images of shape memory effect of PCL/epoxy microfiber membranes: (a) original shape; (b) deformed shape; (c) recovered shape. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the combination of PCL and epoxy exhibited the comprehensive properties and the proportion of core materials and shell materials could be adjusted by changing the electrospinning conditions, such as applied voltages, flow rates as well as tip-to-collector distance.

The nanotension test was performed to obtain the mechanical properties of PCL and PCL/epoxy composite fiber membranes and the results are shown in Table 1. The mechanical strength and the elongation at break were improved by electrospinning composite fibers with core–shell structure. Strain–stress curves of specimens dried for 24 h are shown in Fig. 5b. Strength and elongation at break for PCL/epoxy composite fiber membranes were higher compared to the PCL fiber membranes. The strength increased from 1.78 MPa for PCL to 2.41 MPa for PCL/epoxy caused by epoxy which played a reinforcement role in this system. It could be concluded that the core/shell composite fiber membranes exhibited excellent mechanical properties.

3.4. Shape memory behavior

In order to analyze the shape memory effect of microstructure of electrospun PCL/epoxy fiber membranes, the network of fabricated fiber membranes was investigated using SEM. As shown in Fig. 6, it demonstrates the shape memory recovery process of fibers in microscopic dimensions. The original shape (Fig. 6a) is stretched along the direction of the arrow to fix the temporary shape (Fig. 6b). When heated above the transition temperature, the deformed shape completely recovers to its permanent shape (Fig. 6c). The pore structure of the original shape offered this composite fiber membrane with potential applications in the wider field, especially biomedicine such as tissue engineering. The surface area, pore volume and diameter are listed in Table 2. The BET surface area of core/shell composite fiber membranes induced slightly. The increase of the diameter of composite fibers brought about the change in surface and pore structure, and parameters.

The shape recovery performance of PCL/epoxy composite fiber membranes triggered by heat was investigated using a typical bending method. The specimen with the dimension of 25 mm × 3 mm × 0.5 mm was heated at 70 °C ($T > T_m$) and then bent to a "U" shape. Cooling the sample down to the room temperature ($T < T_m$) was carried out in order to fix the temporary shape. The temperature range above body temperature up to 70 °C was

Table 2
The surface area and pore size of electrospun fiber membranes.

Samples	BET surface area (m^2/g)	Pore volume (cm^3/g)	BJH absorption average pore diameter (4 V/A) (Å)
PCL membranes	6.23	0.0035	40.12
PCL/epoxy membranes	2.94	0.0017	67.61
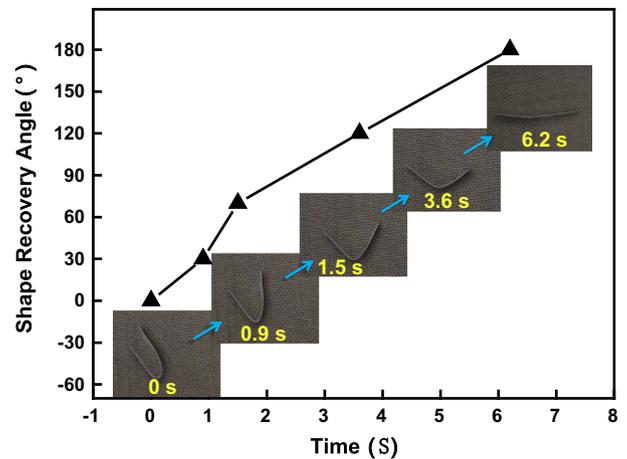
Fig. 7. Shape recovery performances and angles of PCL/epoxy composite microfiber membrane. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

applied to fix the temporary shape and actuate the shape memory effect [18,33,34]. Fig. 7 shows the photographs of the shape recovery process and shape recovery angles vs time. When the deformed "U" shape of composite fiber membrane was subjected to the 70 °C oven, it rapidly unfolded to its original shape "—". Throughout the entire process, the complete shape recovery took only 6.2 s. The shape recovery ratio was approximately 100%. The result of this experiment demonstrated that the electrospun PCL/epoxy composite microfiber membranes with core/shell structure exhibited excellent shape memory behavior. This feature proved the shape
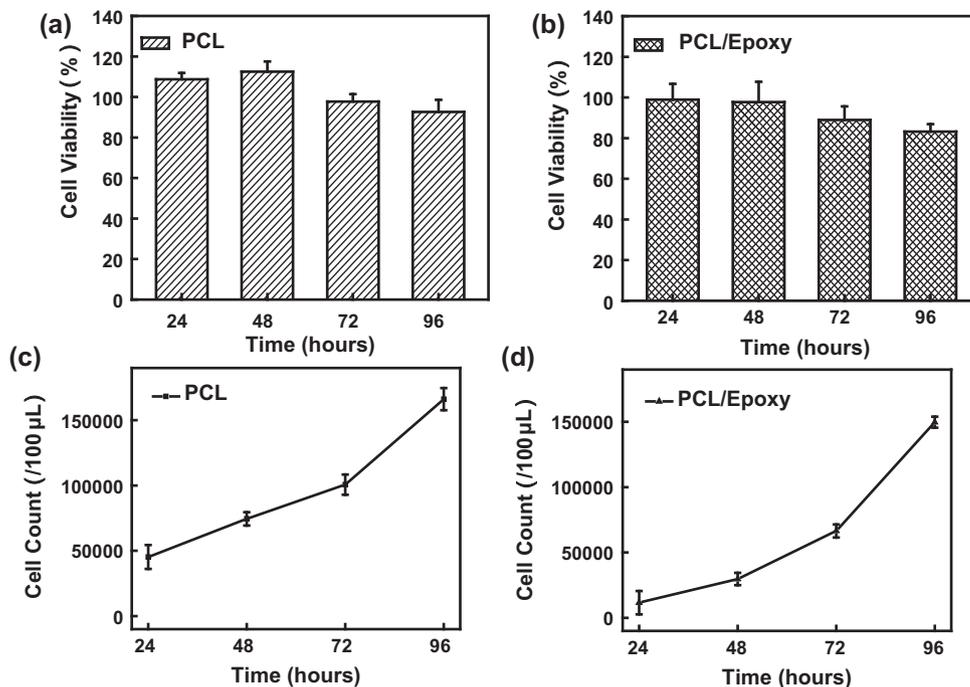
Fig. 8. (a) and (b) the cell viability of electrospun PCL and PCL/Epoxy membranes; (c) and (d) the cell culture on the electrospun PCL and PCL/Epoxy membranes.

memory effect of SMPs: it was able to memorize the temporary shape which recovers quickly above the transition temperature.

3.5. Cytotoxicity analysis

The cytotoxicity of electrospun PCL and PCL/Epoxy microfiber membranes was evaluated by CCK-8 assay. As shown in Fig. 8a and b, the cell viability for both samples was about or more than 100% within 24 h. After 4 days' cultivation, the cell viability on PCL/epoxy membranes did not decrease a lot compared with the pure PCL membrane. The two specimens exhibited better biocompatibility. This result also indicated that the PCL improved the biocompatibility of epoxy through the co-electrospinning process. It can be seen from Fig. 8c and d that the cell amount has an obvious increase during the 4 days' cultivation. The cell viability of PCL/epoxy and PCL membrane was more than 80% on the fourth day, suggesting that they were all non-toxic [32,35].

4. Conclusions

To sum up, a series of deformable, shape memorizing microfiber membranes have been fabricated via coaxial electrospinning. During the electrospinning process, the morphology of the microfibers can be altered by adjusting the feed rate of the core and shell solution. When the core and shell fluid have the appropriate feed rate, the resulting microfibers are continuous and smooth. The PCL/epoxy composite microfibers exhibit the stable core/shell structure. More importantly, the mechanical analysis proves that the strength of composite fiber system is successfully improved compared with pure PCL fibers. The shape memory test indicates the PCL/epoxy composite microfiber membranes possess excellent shape memory effect and high shape recovery speed. The vitro cytotoxicity test shows that the PCL/epoxy composite microfiber is nontoxicity. Our approach to programmable micro-size fiber membranes will be potentially used in various types of thermal responsive smart structures, biomedical or other practical fields.

References

[1] Lendlein A, Langer R. Biodegradable, elastic shape-memory polymers for potential biomedical applications. Science 2002;296:1673–6.
[2] Leng JS, Lan X, Liu YJ, Du SY. Shape-memory polymers and their composites: stimulus methods and applications. Prog Mater Sci 2011;56(7):1077–135.
[3] Lendlein A, Jiang H, Junger O, Langer R. Light-induced shape-memory polymers. Nature 2005;434:879–82.
[4] Xu T, Li GQ, Pang SS. Effects of ultraviolet radiation on morphology and thermo-mechanical properties of shape memory polymer based syntactic foam. Composites Part – A 2011;42:1525–33.
[5] Huang WM, Yang B, Zhao Y, Ding Z. Thermo-moisture responsive polyurethane shape-memory polymer and composites: a review. J Mater Chem 2010;20:3367–81.
[6] Meng QH, Hu JL. A review of shape memory polymer composites and blends. Composites Part – A 2009;40:1661–72.
[7] Diorio M, Luo XF, Lee KM, Mather PT. A functionally graded shape memory polymer. Soft Matter 2011;7:68–74.
[8] Leng JS, Lu HB, Liu YJ, Huang WM, Du SY. Shape-memory polymers a class of novel smart materials. MRS Bull 2009;34:848–55.
[9] Meng H, Li GQ. A review of stimuli-responsive shape memory polymer composites. Polymer 2013;54:2199–221.
[10] Luo XF, Mather PT. Triple-shape polymeric composites (TSPCs). Adv Funct Mater 2010;20:2649–56.
[11] Luo XF, Mather PT. Shape memory assisted self-healing coating. ACS Macro Lett 2013;2:152–6.
[12] Oh HJ, Kim HY, Kim SS. Effect of the core/shell-structured meta-aramid/epoxy nanofiber on the mechanical and thermal properties in epoxy adhesive composites by electrospinning. J Adhes 2014;90:787–801.
[13] Oh HJ, Han SH, Kim HY, Kim SS. The influence of the core–shell structured meta-aramid/epoxy nanofiber mats on interfacial bonding strength and the mechanical properties of epoxy adhesives at cryogenic environment. J Adhes Sci Technol 2014;10:950–62.
[14] Li D, Xia YN. Electrospinning of nanofibers: reinventing the wheel. Adv Mater 2004;16:1151–70.
[15] Huang ZM, Zhang YZ, Kotaki M, Ramakrishna S. A review on polymer nanofibers and their applications in nanocomposites. Compos Sci Technol 2003;63:2223–53.
[16] Greiner A, Wendorff JH. Electrospinning: a fascinating method for the preparation of ultrathin fibers. Angew Chem 2007;46:5670–703.

[17] Cipitria A, Skelton A, Dargaville TR, Daltona PD, Hutmacher DW. Design, fabrication and characterization of PCL electrospun scaffolds-a review. J Mater Chem 2011;21:9419–53.

[18] Gong T, Li WB, Chen H, Wang L, Shao S, Zhou SB. Remotely actuated shape memory effect of electrospun composite nanofibers. Acta Biomater 2012;8:1248–59.

[19] Meng QH, Hu JL, Zhu Y, Lu J, Liu Y. Morphology, phase separation, thermal and mechanical property differences of shape memory fibres prepared by different spinning methods. Smart Mater Struct 2007;16:1192–7.

[20] Zhuo HT, Hu JL, Chen SJ. Electrospun polyurethane nanofibres having shape memory effect. Mater Lett 2008;62:2074–6.

[21] Zhang FH, Zhang ZC, Liu YJ, Lu HB, Leng JS. Quintuple-shape memory effect in electrospun nanofiber membranes. Smart Mater Struct 2013;22:085020.

[22] Zhang FH, Zhang ZC, Liu YJ, Leng JS. Shape Memory properties of electrospun Nafion nanofibers. Fibers Polym 2014;15:534–9.

[23] Chen HL, Cao XY, Zhang JN, Zhang JJ, Ma YM, Shi GQ, et al. Electrospun shape memory film with reversible fibrous structure. J Mater Chem 2012;22:22387–91.

[24] Matsumoto H, Ishiguro T, Konosu Y, Minagawa M, Tanioka A, Richau K, et al. Shape-memory properties of electrospun non-woven fabrics prepared from degradable polyesterurethanes containing poly(omega-pentadecalactone) hard segments. Eur Polym J 2012;48:1866–74.

[25] Kotek R. Recent advances in polymer fibers. Polym Rev 2008;48:221–9.

[26] McDowell JJ, Zacharia NS, Puzzo D, Manners I, Ozin GA. Electroactuation of alkoxysilane-functionalized polyferrocenylsilane microfibers. J Am Chem Soc 2010;132:3236–8.

[27] Zhuo HT, Hu JL, Chen SJ. Coaxial electrospun polyurethane core-shell nanofibers for shape memory and antibacterial nanomaterials. Express Polym Lett 2011;5:182.

[28] Sun ZC, Zussman E, Yarin AL, Wendorff JH, Greiner A. Compound core–shell polymer nanofibers by co-electrospinning. Adv Mater 2003;15:1929–32.

[29] Leng JS, Wu XL, Liu YJ. Effect of a linear monomer on the thermomechanical properties of epoxy shape-memory polymer. Smart Mater Struct 2009;18:095031.

[30] Decker. Photoinitiated crosslinking polymerization. Prog Polym Sci 1996;21:593–650.

[31] Lu HB, Gou JH, Leng JS, Du SY. Magnetically aligned carbon nanotube in nanopaper enabled shapememory nanocomposite for high speed electrical actuation. Appl Phys Lett 2011;98:174105.

[32] Zhou M, Wang WC, Liao YG, Liu WQ, Miao YU, Ouyang CX. In vitro biocompatibility evaluation of silk-fibroin/polyurethane membrane with cultivation of HUVECs. Front Mater Sci 2014;8(1):63–71.

[33] Cha DI, Kim HY, Lee KH, Jung YC, Cho JW, et al. Electrospun nonwovens of shape-memory polyurethane block copolymers. J Appl Polym Sci 2005;96:460–5.

[34] Matsumoto H, Ishiguro T, Konosu Y, Minagawa M, Tanioka A, et al. Shape-memory properties of electrospun non-woven fabrics prepared from degradable polyesterurethanes containing poly(x-pentadecalactone) hard segments. Eur Polym J 2012;48:1866–74.

[35] Chang YL, Yang ST, Liu JH, Dong E, Wang YW, Cao A, et al. In vitro toxicity evaluation of graphene oxide on A549 cells. Toxicol Lett 2011;200:201–10.